

REMARKS

Claims 1-8 and 15-25 are pending in the application. Claims 1-8, 15-18 and 20-25 are rejected. Claim 19 is objected to. Claim 1 has been amended for clarity according to Applicants' Remarks of 26 January 2004 by stating that the polymer of the present invention excludes those amide polymers wherein the N in the side chain is linked to the backbone. New claim 26 has been added, which is the combination of claims 1 and 19 that the Examiner has indicated to be allowable subject matter. Accordingly, no new matter is introduced by these amendments.

Reply to the Rejection of Claims 1-4, 6-8 and 20-25 under 35 U.S.C. § 102(b) or 103(a)

The Examiner has rejected Claims 1-4, 6-14 and 20-25 as being anticipated by U.S. Patent No. 5,843,192 to Kirk *et al.* ("Kirk") or, alternatively, rendered obvious in view of Kirk. Specifically, the Examiner states –

Kirk *et al* teach a composition useful in a washing process containing at least on vinyl amide polymer. The vinyl amide polymer contains from 5 to 100 weight percent of at least one vinyl amide monomer, and from 0 to 95 weight percent of one or more vinyl ester monomers. Kirk *et al* also provides a method of cleaning an article and a method of providing soil resistance to an article using the vinyl amide polymer. See Abstract. The vinyl amide polymer preferably contains less than 3 weight percent of one or more ethylenically unsaturated carboxylic acid monomers, based on the total weight of the monomers. The carboxylic acid monomers include acrylic acid, methacrylic acid, maleic acid, itaconic acid, etc. The vinyl amide polymer preferably contains less than 3 weight percent of one or more acrylamide monomers. Suitable acrylamide monomers include acrylamide, N,N-dimethylacrylamide, acrylamidoalkylenesulfonic acid, etc. See column 4, lines 30-50. The cleaning solution may optionally contain additional components such as surfactants, builders, buffering agents, bleaching agents, enzymes, perfumes, etc. See column 5, lines 1-35. The treatment solution is contacted with the article by immersing the article with the solution. See column 6, lines 25-45.

Specifically, Kirk *et al* teach a composition containing 8% linear alkyl benzene sulfonate, 16% alcohol ether sulfate, 6% nonionic surfactant, 0.5% enzyme, 2% vinyl amide polymer, etc. See column 14, lines 50-69. Note that, the Examiner maintains that the vinyl amide polymer would inherently have the same mole percent of amide monomer as recited by the instant claims. Accordingly, the broad teachings of Kirk *et al* are sufficient to anticipate the material limitations of the instant claims.

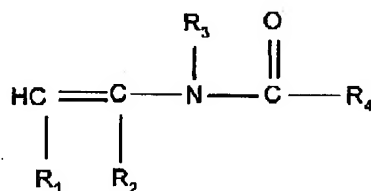
Alternatively, even if the broad teaching of Kirk *et al* are not sufficient to anticipate the material limitations of the instant claims, it would have been

nonetheless obvious to one of ordinary skill in the art to arrive at the claimed mole percent of amide polymer of the composition in order to provide the optimum soil resistant properties to the composition since Kirk et al teach that the amount and type of amide used in formulating the resultant polymer may be varied. . . .

. . . With respect to Kirk et al, Applicant states that unlike the vinyl amide (*sic*, amide) monomers of Kirk et al, the amide monomers as recited by the instant claims are free of amine linkages in the side chain. Additionally, Applicant states that the amide monomer side unit is in an amount of at least five mole percent while the optional acrylamides of Kirk are limited to an amount of less than three weight percent. In response, note that the instant claims require that the polymer has "at least five mole percent, based on the total mole percent of the polymer, of one or more amide monomer units". The Examiner maintains that the teaching of Kirk et al which requires that the polymer comprises 5 to 100 weight percent of at least one vinyl amide monomer would meet the vinyl amide monomer limitation as recited by the instant claims. Additionally, note that, Kirk et al (*sic, et al.*) do not required (*sic*, require) the presence of any amine linkages in the side chains as recited by the instant claims. The Examiner sees no distinction between the polymers of Kirk et al and those recited by the instant claims.

For the following reasons, Applicants respectfully traverse the Examiner's rejection of claims 1-4, 6-8 and 20-25 as being anticipated by Kirk.

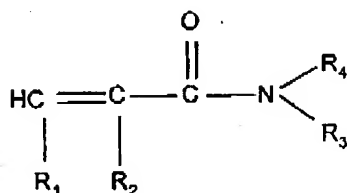
As previously indicated, Kirk teaches a composition useful in a washing process containing at least one vinyl amide polymer having 5-100 weight % of at least one vinyl amide monomer, and 0-95 weight % of one or more vinyl ester monomers, and an additive (Abstract; col. 2, lines 28-49). The at least one vinyl amide monomer required in the composition of Kirk is of the formula –



(col. 3, lines 12-36; claim 1). This required monomer clearly illustrates an amide monomer having a nitrogen linkage linked to the polymer backbone.

Preferably, the vinyl amide polymer contains less than three (3) weight percent of one or more ethylenically unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acids and salts thereof (col. 4, lines 33-38; claim 1). The vinyl amide

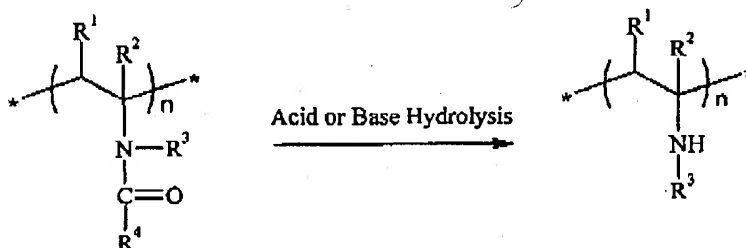
polymer also preferably contains less than three (3) weight percent of one or more acrylamide monomers of the formula –



(col. 4, lines 39-55; claim 1). Examples of such acrylamide monomers include N,N-dimethyl acrylamide. (In contrast, see Example 1 of the present description wherein the N,N-dimethyl acrylamide is present in the polymer in an amount of 90%.)

The washing composition of Kirk includes a vinyl amide polymer in a weight percentage of 0.01 to 20 weight % of the composition. This vinyl amide polymer is formed from 5 to 100 weight percent of a vinyl amide monomer and from 0 to 95 of a vinyl ester monomer. The polymer can also optionally include acrylamide monomers in an amount of less than 3 weight percent. Carboxylic acid monomers can be optionally found in the polymer in an amount of less than 3 weight percent.

It is well known that vinyl amide based polymers such as the required vinyl amide polymers of Kirk easily hydrolyze under both acid and base conditions as follows –

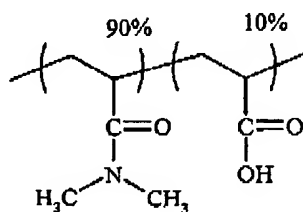


For example, polyvinyl formamide (a polyvinyl amide) is known to readily hydrolyze to polyvinyl amines in acidic or basic solution (see, Stinson, Stephen, *Quest for commercial polyvinylamine advances*, CHEMICAL & ENGINEERING NEWS, p. 32, Sep. 6, 1993 (stating that “polyvinylformamide is readily hydrolyzed to [polyvinyl amine] in acidic or basic solution”), attached hereto as Exhibit A). N-ethyl formamide is also known to readily hydrolyze under such conditions (see, Badesso, R.J. *et al.*, *Synthesis of Amine Functional Homopolymers with N-*

Ethenylformamide, POLYMER PREPRINTS, vol. 34, pp. 251-52 (1993) (stating that a "particular advantage of [N-ethenylformamide] is the ease of hydrolysis of its polymers"); *see also*, Badesso, R.J. *et al.*, *High and Medium Molecular Weight Poly(vinylamine)*, POLYMER PREPRINTS, vol. 32, pp. 110-11 (1991), attached hereto as Exhibit A). Col. 3, lines 34-36 of Kirk indicates that N-vinyl formamide is an example of its required vinyl amide monomers. As such, this hydrolysis is recognized as a commercial route to polyvinyl amine.

Most cleaning compositions or formulations contain either an acid or a base. Accordingly, polyvinyl amide polymers such as those described in Kirk will hydrolyze in these cleaning formulations during storage and in end use, losing performance over time.

In contrast to Kirk, the amide polymers of the present invention are attached to the polymer backbone by the carbonyl group (C=O) and not by the nitrogen linkages as is the case with polyvinyl amide polymers. For example, the following illustrates an amide polymer according to the present invention (exemplified in Example 1 of the present description) –



Example 1 - copolymer of N,N-dimethyl acrylamide (90 mole %) and acrylic acid (10 mole %)

Therefore, the amide polymers of the present invention are not subject to the relatively facile hydrolysis that polyvinyl amide polymers undergo. As such, the amide polymers of the present invention do not lose performance during storage or in the washing process.

Example 13 of the present description illustrates use of the polymer according to the present invention in acidic and alkaline hard surface cleaning formulations. Polyvinyl amide polymers such as those taught by Kirk will hydrolyze to polyvinyl amine under these pH conditions. The resultant polyvinyl amine will protonate, developing a positive charge (see Graph 2 of the 1991 Badesso article attached hereto illustrating that protonation occurs over a pH range of from about 2 to about 10). It will then attract negatively charged soils such as soap scum, instead of repelling them in the bathroom cleaner application. In contrast, polymers according to the present invention remain neutral under these pH conditions, repelling soils such

as soap scum. Kirk does not teach or suggest use of its polymers in an acidic bathroom cleaner, nor does it teach or suggest a bathroom cleaner formulation having acid(s) in its list of ingredients.

Regarding the Examiner's remarks that "the vinyl amide polymer would inherently have the same mole percent of amide monomer as recited by the instant claims", Applicants respectfully disagree. Kirk states that its vinyl amide polymer "is formed from 5 to 100 weight percent, preferably from 15 to 70 weight percent, and most preferably 20 to 40 weight percent of the vinyl amide monomer [of Formula (I)] based on the total weight of monomer used to form the vinyl amide polymer" (col. 3, lines 37-41). As previously indicated to the Examiner and as further clarified in the present amendment to claim 1, the amide monomer(s) is free of amine linkages linked to the polymer backbone in the side chains. Therefore, the 5 to 100 weight percent of vinyl amide polymer according to Formula I of Kirk is not equivalent to the 5 to 100 weight percent of amide monomer units without an amine linkage to the polymer backbone as claimed in claim 1 of the present invention.

Unlike the vinyl amide monomers of Kirk, the amide monomers of the present invention are free of nitrogen linkages in the side chain. Accordingly, as Kirk does not teach or suggest a polymer comprising an amide monomer free of nitrogen linkages linked to the polymeric backbone and in an amount of at least five mole percent, Kirk cannot be said to anticipate the present surface protection composition.

It is believed that these remarks overcome the Examiner's rejection of claims 1-4, 6-14 and 20-25 as being anticipated by Kirk under 35 U.S.C. § 102(b) or, alternatively, rendered obvious in view of Kirk under 35 U.S.C. § 103(a). Withdrawal of the rejection is respectfully requested.

Reply to the Rejection of Claims 5 and 15-18 under 35 U.S.C. § 103(a)

The Examiner has rejected Claims 5 and 15-18 as being unpatentable over Kirk. Specifically, the Examiner states –

Kirk et al are relied upon as set forth above. However, Kirk does not specifically teach a polymer treated substrate having associated thereon a polymer containing an amide monomer and the other requisite components of the composition in the specific proportions as recited by the instant claims.

It would have been obvious to one of ordinary skill in the art, at the time the invention was made, to formulate a polymer treated substrate having associated thereon a polymer containing an amide monomer, a hydroxyl alkyl urea monomer, and the other requisite components of the composition in the specific proportions as recited by the instant claims, with a reasonable expectation of success and similar results with respect to other disclosed components, because the broad teaching of Kirk et al suggest a polymer treated substrate having associated thereon a polymer containing an amide monomer, a hydroxyl alkyl urea monomer, and the other requisite components of the composition in the specific proportions as recited by the instant claims. . . .

. . . .With respect to the amount of acrylamide monomer units, instant claim 5 recites that the monomer units further comprise monomer units such as N,N dimethylacrylamide and does not require that these acrylamide monomers are present in any specific amounts; the Examiner maintains that less than 3 weight percent of acrylamide monomers would meet the limitations as recited by instant claim 5.

For the following reasons, Applicants respectfully traverse the Examiner's rejection of claims 5 and 15-18 as being unpatentable over Kirk.

As noted above, Kirk requires a vinyl amide monomer according to its Formula I in an amount of 5 to 100 weight percent based on the total weight of monomer used to form the vinyl amide polymer. This required vinyl amide monomer contains an amine (N) linkage linked to the polymer backbone in its side chain. In contrast, the polymer of the present invention is free of amine linkages in the side chain. Accordingly, as Kirk does not teach or suggest a polymer comprising an amide monomer free of nitrogen linkages and in an amount of at least five mole percent, Kirk cannot be said to render obvious the present surface protection composition.

It is believed that these remarks overcome the Examiner's rejection of 5 and 15-18 as being unpatentable over Kirk under 35 U.S.C. § 103(a). Withdrawal of the rejection is respectfully requested.

Based on the above amendments and remarks, allowance of the claims is believed to be in order, and such allowance is respectfully requested.

Respectfully submitted,

Dated: 1 July 2004
NATIONAL STARCH AND CHEMICAL COMPANY
Post Office Box 6500
Bridgewater, New Jersey 08807-0500
Phone 908.683.5433
Fax 908.707.3706

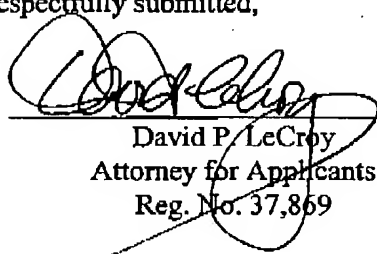

David P. LeCroy
Attorney for Applicants
Reg. No. 37,869

Exhibit A

SCIENCE/TECHNOLOGY

tures to yield pure isobutene and regenerate glycol. Among the advantages to this approach are that the catalyst is a solid, no solvents are involved, and because of catalyst selectivity there are no equilibrium limitations.

A typical C₄ stream that would be treated in this way is the refinery stream often designated as "Raffinate-1." This stream would contain, say, 12.7% isobutene, 12.2% 1-butene, 13.4% *cis*-2-butene, 17.5% *trans*-2-butene, 10.8% isobutane, and 31.6% *n*-butane, the remainder being miscellaneous C₄ compounds.

Classes of solid acid catalysts that would be suitable for use in the processing include acidified montmorillonite clays and heteropoly acids dispersed on Group IV oxides. Knifton notes that a Japanese group has proposed a similar process using sulfonic acid organic resins as catalysts. He believes the Texaco process works better because the Texaco catalysts have higher thermal stability, particularly at temperatures higher than 120 °C—the preferred temperature for de-etherification.

In a typical pilot test of the Texaco

process, Raffinate-1 feedstock and 1,2-propylene glycol were fed separately to a 50-cc plug-flow reactor charged with 12-tungstophosphoric acid on titania as the catalyst. Etherification to generate propylene glycol *tert*-butyl ethers occurred at temperatures between 60 and 120 °C. All effluent products appeared in two layers. Data indicated up to a 44% conversion of the isobutene fraction to propylene glycol mono *tert*-butyl ethers. The principal product is 1-butoxy-2-propanol with smaller quantities of 2-butoxy-1-propanol. The other C₄ olefins do not undergo significant etherification. Montmorillonite clays also function as catalysts but are generally less effective than the heteropoly acids.

The heavier glycol phase was separated from the lighter Raffinate-1 phase and passed, separately, through a similar 50-cc reactor charged with fresh catalyst. De-etherification of the glycol *tert*-butyl ether intermediates to produce pure isobutene plus glycol to be recycled occurs at higher reaction temperatures over the same classes of solid acid catalysts.

Joseph Haggin

responding polyvinylformamide is readily hydrolyzed to PVAm in acidic or basic solution.

Working with Richard J. Badesso and Dennis J. Sagi, Pinschmidt makes *N*-vinylformamide by pyrolysis of ethylideneformamide, $\text{CH}_3\text{CH}(\text{NHCHO})_2$, which in turn comes from acid-catalyzed condensation of formamide with acetaldehyde. The researchers have developed a series of solution and emulsion polymerizations of *N*-vinylformamide that give molecular weights of 2 million to 4 million, 300,000 to 500,000, and 50,000. These differing molecular weights yield a range of materials to try in different applications.

Some of the situations met in making PVA_m give a preview of the interesting properties that await users. For example, acid-catalyzed hydrolysis of polyvinylformamide proceeds to only 65% completion because of the intense positive charge building on the resin chains.

Base-catalyzed hydrolysis, on the other hand, can be 100% complete. But because the formula weight of formates liberated (45) is comparable to the formula weight of vinylamine repeating units (43), large amounts of formate salts remain in intimate association with the resin. The Air Products team has succeeded in removing formates by dialysis or by precipitation from butanol solutions of the resin. Other, cheaper, more convenient ways to produce resins free of formates are in progress, Pinschmidt says.

Some past efforts of other researchers give an idea of the fervor with which PVAm has been pursued. Polymerization of *N*-vinylphthalimide followed by hydrazinolysis succeeded, but at great expense. *N*-Vinylacetamide was cheaper, but hydrolysis conditions were severe.

By contrast, *N*-vinylformamide is quite tractable. It is a liquid with negligible vapor pressure at room temperature that distills at 84 °C under 10 mm Hg, which corresponds to an atmospheric boiling point of 210 °C. It can be stored for months at room temperature. Its LD₅₀ (the dose that is lethal to 50% of a population in an acute toxicity test) of 1444 mg per kg in rats indicates low toxicity. Such azo compounds as azobis(isobutyronitrile) are best as initiators, whereas persulfates generate acidity that could lead to explosions.

Stephen Stinson

Quest for commercial polyvinylamine advances

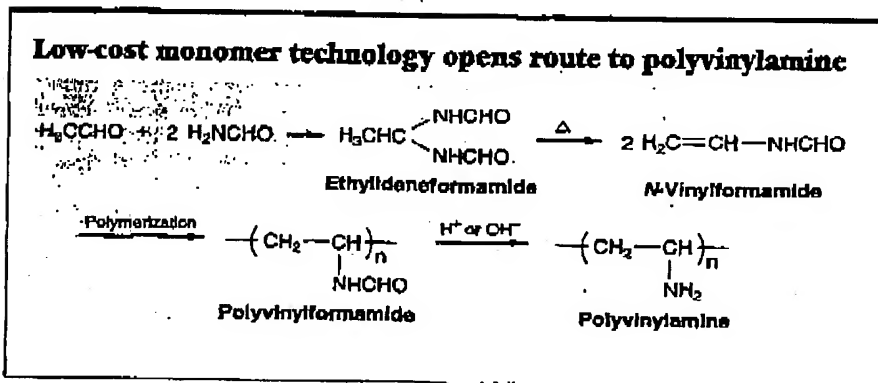


For some years, chemists have been trying to find a way to turn polyvinylamine (PVAm) into a commercial product. Researchers at Air Products & Chemicals report progress in that quest.

Beckoning chemists in their decades-long interest is the potential of a product with the high density of very polar,

Lewis-basic amino groups, which could have useful interactions with other substances. Thus, PVAm could find uses in water treatment, papermaking, textile finishes, personal care products, adhesives, coatings, and oil field chemicals. The trick is to produce it easily and inexpensively.

As research chemist Robert K. Finschmidt Jr. told the Division of Polymeric Materials: Science & Engineering, the key to success thus far has been making and working with *N*-vinylformamide monomer, $\text{CH}_2=\text{CHNHCHO}$. The cor-

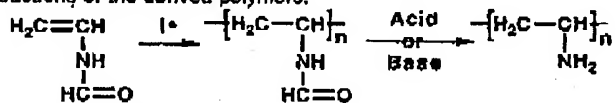


Synthesis of Amine Functional Homopolymers with N-Ethenylformamide

R. J. Badesso, R. K. Pinschmidt, Jr., D. J. Sagi
Corporate Science and Technology Center
Air Products and Chemicals, Inc.
7201 Hamilton Blvd., Allentown, PA 18195

Introduction

Practical, low cost synthesis of polymers and copolymers containing stable primary amine functionality has been a dream of polymer chemists for generations. Reduction to practice has been severely constrained by the instability or poor polymerizability of amine containing vinyl monomers. Only polymerization of aziridine to a mixture of primary, secondary and tertiary amine has achieved significant commercial success. With the development of N-ethenylformamide (NEF), a readily hydrolyzable blocked vinylamine monomer, this goal now appears at hand. Handling, homopolymerization and hydrolysis issues in the successful preparation of amine and amide functional polymers is reported, along with some of the widely variable properties, structure and reactions of the derived polymers.



N-Ethenylformamide [NEF] Poly(ethenylformamide) [PEF] Poly(vinylamine) [PVAm]

Mol. Wgt 71.02

Experimental

NEF (N-ethenylformamide) is prepared via the vapor phase pyrolysis of ethyldenebisformamide and purified via fractional distillation. Other reagents were obtained from commercial sources and used without further purification.

Earlier [1] solution and inverse emulsion polymerizations of NEF have been improved.

Inverse Emulsion PEF. ($M_w = 2.4 \times 10^5$). Using a cylindrical reactor at 40-55°C with dual-blade stirrer at 2000 rpm, sorbitan monostearate (3 wt%) was dissolved in cyclohexane (51%) under nitrogen. Nitrogen sparged NEF (25%) plus water (21%) were added gradually to establish the inverse emulsion. Vazo-52 [2,2'-azobis(2,4-dimethylpentanenitrile)] (0.05 wt%) was added. After 5 h the temperature was increased slowly to 55°C and held 5 h. A free-flowing PEF granular powder could be recovered by simply drying the emulsion. Surfactant may be removed by washing the solid polymer with ethyl acetate.

p-Ethenylformamide (PEF). $M_w = 300,000$ to $500,000$ may be prepared by sparging a 15 wt% solution of NEF in water (pH 8 with ammonia) with nitrogen at 20°C with agitation, followed by adding 2,2'-azobis(N,N'-dimethylethylisobutyramidine-2-HCl) [VA-044, Wako], 0.1% [0.2 mole % on monomer]. After 1 h, the temperature was raised to 55°C over 60 min and maintained for 4 h, then increased to 60°C for one h to complete the reaction. The MW may be raised to 700,000 by polymerizing a 20% NEF solution at 45°C, but the reaction must be diluted to 10% solids at high conversion to maintain agitation. The polymer may be hydrolyzed *in situ* or recovered by precipitation with nonsolvents such as MeOH, IPA or acetone.

PEF $M_w = 50,000$ was prepared by delay feeding a nitrogen sparged 20% aqueous solution of NEF and 1 mol% V-60 to the reactor under nitrogen at 80°C.

Precipitation Polymerization to Low MW. NEF, 21.5 wt%; isopropanol, 61.2%; toluene, 16.9%; and Vazo 52, 0.4%, were sparged with nitrogen and heated to 65°C over 35 min under rapid stirring. After 2 h at 65°C, free-flowing PEF powder was isolated by filtration and drying. Medium MW was obtained by substituting t-butanol for the above solvents and using half the level of Vazo-52 (6.5 h reaction).

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Hydrolysis. Base hydrolysis of PEF has been reported [1]. Acid hydrolysis of 10 (MMW) - 20% (LMW) aqueous solutions of PEF with HCl goes to 65% conversion in 6 h at 80°C. Samples were isolated as in [1]. PEF, including high MW PEF, powder suspensions (20-25 wt%) in cyclohexane or 1.5:1 cyclohexane/BuOH may be hydrolyzed to any desired level by adding the calculated amount of dry KOH or NaOH slowly and mixing for 4-6 h at 70°C. The solid product contained both dry polymer and formate salt.

Salt-Free LMW p-Vinylamine. A 30 wt% slurry of LMW PEF powder in butanol was hydrolyzed to the desired degree with powdered NaOH for 7-8 h at 80°C with moderate stirring (longer times beyond 85% hydrolysis). It is important to minimize the amount of moisture in the reaction if formate salt is to be removed as a dry solid. At the end of the reaction the suspended solid Na formate was removed from the dissolved PVAm solution polymer by centrifugation and the solution was concentrated on a rotary evaporator at 45-50°C. The resulting oil was further dried at 25 torr, frozen with liquid nitrogen, ground to a granular polymer and again dried.

Dialysis. Cellulose acetate dialysis tubing with a MW cutoff of 6000-8000 was filled halfway with medium MW base hydrolyzed PVAm. The mixture was dialyzed at room temperature for 2-3 days against 4-5 times the polymer solution volume of distilled or deionized water, which was changed two times per day.

Salt-Free High MW PVAm. High MW PEF powder was allowed to swell in a 2X excess of water at 60°C while stirring gently. The gel was then diluted to 15 wt% with acetone and again stirred gently. The PVAm precipitated as a solid slab, leaving NaHCOO in solution. The isolated slab was washed with 2:1 acetone/water, vacuum dried at 45°C and ground. The powder was rewashed and vacuum dried as above.

Analytical. NEF may be characterized by gas chromatography (25m fused silica 3% OV-1701 column, 3 min/80°C + 15°C/min ramp to 200°C). NEF response becomes severely non-linear at low sample sizes and small quantities of the dimer are not completely stable under GC conditions.

NEF monomer levels of 0.005 to 0.10% in polymers may also be assayed by ultraviolet spectroscopy by extracting 10 g of powdered polymer with 100 ml of acetonitrile, diluting by a factor of 10 and measuring the absorbance at the λ_{max} of 224 nm (13,000) vs a standard.

¹H NMR, (neat vs D₂O capillary) δ 4.60 (d, 1H, J = 8.7 Hz), 4.92 (dd, 1H, J = 1.2 Hz, J = 8.8 Hz), 5.13 (d, 1H, J = 15.4 Hz), 5.23 (d, 1H, J = 15.9 Hz), 7.08 (ddd, 1H, J = 8.7 Hz, J = 10.7 Hz, J = 15.6 Hz), 7.24 (dddd, 1H, J = 0.44 Hz, J = 8.8 Hz, J = 10.6 Hz, J = 15.9 Hz), 8.68 (s, 1H), 8.78 (d, 1H, J = 11.3 Hz), 8.99 ppm (br s, 1H).

¹H NMR of PEF: δ (D₂O): 1.50 (br s, 2H, methylene), 3.22, 3.3 (2 low, br s, -0.15H) + 3.75 (br s, 0.85H, methine), 4.60 (NH + HOD) and 7.46, 7.6, 7.68 (m, 0.15H) + 7.8 ppm (6 line m, 0.85H, formyl H) (total = 1.05H vs methylenes in 8 samples).

¹³C NMR of PEF: δ (D₂O) 37.5-41 (m, 1C, methylene), 41-42.3 (m, -0.85C), 46.5-48.5 (m, -0.15C, head-to-head methine?), 163.6 (s, -0.85C, formyl), and 166-167.6 ppm (m, -0.15C, formyl). This may represent about 15% head-to-head polymer.

NMR spectra of PEF and PVAm have been reported [2-4].

Results and Discussion

NEF is a highly reactive, but reasonably stable, low volatility liquid with excellent polymerizability and copolymerizability. Despite its low volatility, the molecular weight is only 71, giving 20% nitrogen on a weight basis (37% NH₂ after hydrolysis and formate removal). This offers an extremely high ionic content in homopolymers and a high level of amine or amide functionality per pound relative to other functional monomers. Toxicity and environmental impacts appear minimal (LD50(rat) = 1,444 mg/kg). It is a vacuum distillable liquid. N-Ethenylformamide is quite stable for many months at room temperature when sufficiently pure. Slightly less pure NEF will give at least three months shelf life at 25°C with less than two percent dimer or polymer formation, but is best stored below room temperature in the dark for maximum color stability and purity. It should not be stored above 40°C. As expected for the monomer precursor of an easily hydrolyzed amide polymer, it is sensitive to

bases and, more particularly, highly sensitive to acids. Concentrated monomer plus even small amounts of strong acids may give strongly exothermic reaction with significant gas evolution. Even storage in slightly acidic phenolic lined containers will produce unacceptable dimer and oligomer formation.

Polymerization. NEF can be polymerized to poly(ethenylformamide) (PEF) in high conversion and molecular weight. As with other monomers, chain transfer to solvent has a major impact on ultimate molecular weight. Conversion and ultimate molecular weight are also a strong function of monomer purity, with $M_w > 2 \times 10^6$ obtainable under inverse emulsion conditions with NEF [1]. It is highly stable in water at pH 6-8; however, monomer hydrolysis increases outside this range, particularly with declining pH. (Half-life at pH 4 is greater than 500 min at 60°C.) Water is the best solvent for the homopolymers and the one with the lowest chain transfer constant. Polydispersities are typically around 2-2.5. Other solvents, e.g., t-BuOH, MeOH, toluene, 2-propanol (in declining order of product polymer molecular weight) and solvent mixtures are useful for preparing precipitation polymers of this monomer.

NEF is readily polymerized by free radical initiators such as azo, peroxy and redox types. Peroxides, however, should be avoided because of undesirable side reactions which frequently produce pH drop and severe inhibition of polymerization (also seen with N-vinylpyrrolidone and N-vinylacetamide).

Hydrolysis. A particular advantage of NEF is the ease of hydrolysis of its polymers. Homopolymer PEF easily undergoes 60-70% hydrolysis with stoichiometric acid and mildly elevated temperatures (80°C/6 h), but hydrolysis slows down due to charge repulsion when pushed to high conversion (low vinylamide copolymers are less of a problem). Base hydrolysis suffers no such limitation and full hydrolysis is readily obtained with near stoichiometric levels of hydroxide (e.g., 80°C/8 h). Partial hydrolysis with water alone has also been observed at elevated temperatures under pressure.

Acid hydrolysis generates poly(vinylamine) (PVAm) acid salt and an equivalent of formic acid coproduct, while base produces an equivalent of formate salt. Such coproducts are of minimal concern where the polymer is used at low add-ons, for instance in paper or water treatment, but the extremely high amine level in PVAm (amine equivalent weight = 43) means that the weight of HCOOH or formate salt at full hydrolysis is higher than the weight of PVAm in the homopolymer. Several methods are under development to deal with this issue. At present, one may use dialysis of aqueous samples or procedures (experimental) based on the high solubility of PVAm free base in alcohol.

Polymer Properties. PEF and PVAm·HCl are soluble in water, formamide, ethylene glycol, dimethylsulfoxide at elevated temperature and some water/alcohol mixtures, but not in other common solvents. PVAm free base is similar to PEF, except that lower MW forms are also soluble in methanol or 2-propanol.

Reactive Chemistry: Crosslinking. The primary amino group in PVAm or partially hydrolyzed PEF is highly reactive for crosslinking or derivatization. Examples include reaction with acids, metal cations, epoxies, aminoplasts, isocyanates, anhydrides, aldehydes, lactones and Michael acceptors. PVAm can be crosslinked over a wide pH range with diisocyanates, epichlorohydrin, dialdehydes, glyoxal, diacrylates, and di- and tri-valent anions. PVAm also forms insoluble polyelectrolyte complexes with anionic polymers such as poly(acrylic acid). PEF also complexes with PAA.

Uses. PEF and its hydrolysis products are of interest in water treatment, papermaking, textiles, personal care, adhesives and coatings, rheology modifiers and in oil field chemicals.

Analytical. Unlike higher analogs, NEF monomer is a slowly interconverting 3:1 mixture of two carbonyl-nitrogen bond rotamers on the NMR time scale, giving rise to a surprisingly complex proton NMR. The spectrum can be coalesced at elevated temperatures. The homopolymer likewise shows additional signals and integration of the $\delta 3.71$ peak is consistently low (14-18%) without the 3.1-3.4 ppm peaks. The ^{13}C spectra show similar effects, also not seen in higher analogs, e.g., p-vinylacetamide [2-4]. This may represent a significant level of head-to-head polymer in NEF derived samples.

Acknowledgement: The invaluable assistance of K. Feehan, E. A. Smith and S. R. Salvanovich is gratefully acknowledged.

References

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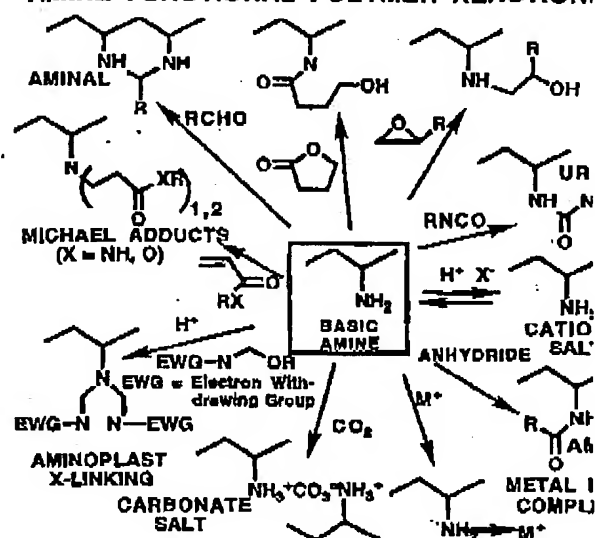
NEF Physical Properties

Bolling Point, @ 13.3 mbar (10 torr)	8
	(theor. 210°C @ 760 t)
Melting Point, °C	-
Density, g/ml @ 25°C	1.1
Vapor Pressure, mbar @ 25°C	<0.1
Flash Point, °C (ASTM D-3828)	-
ΔH Polymerization, kJ/mole	-
	kcal/mole
Tg Homopolymer (300-400k M_w), °C	-
Miscibility	All common solvents (limited with alkane)

Table II Typical Polymer Properties

	Poly(ethenyl formamide) (PEF)			Poly(vinyl amine)-1		
$M_w \times 10^3$ (GPC)	50-100	300-400	1000-3000	50-100	300-400	1000-
Intrinsic Viscosity, $[\eta]$ (dL/g)	0.3-0.4	1.0-1.5	3.0-4.0	0.2-0.3	0.9-1.1	2.1-
Viscosity, cps 5% aq. sol. 20°C, Brookfield	6-10	70-80	2500-3500	5-9	60-75	2000-
Tg by DSC, °C	140	147	150	Decomposition obsci from 220-250°C		
pH, 5% Aqueous Solution @ 20°C	5.5-6.5			2-3		

AMINE FUNCTIONAL POLYMER REACTION:

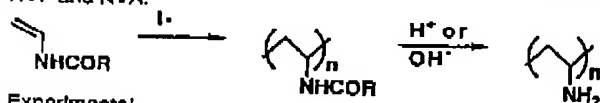


HIGH AND MEDIUM MOLECULAR WEIGHT POLY(VINYLAMINE)
R. J. Badesso, T. W. Lai, R. K. Pinschmidt*, Jr., D. J. Sagl and B. R.
Vijayendran
Air Products and Chemicals, Inc.
Allentown, PA 18195

Introduction

Efficient, cost effective synthesis of high molecular weight polymers with a high level of hydrolytically stable cationic charge or reactive amine functionality has significantly lagged technology for preparing neutral or anionic polymers.

A long standing target in this field has been the simplest and most chemically reactive member, polyvinylamine (PVAm). Although frequently reported in the general [1,2] and patent literature, PVAm has proved a surprisingly elusive target in terms of practical, flexible synthesis. N-Vinylacetamide (NVA) or, preferably, N-vinylformamide (NVF) as precursors appear to solve the practical problems associated with implementing this technology. NVF in particular, although difficult to prepare cleanly, polymerizes and copolymerizes readily to high or low molecular weight polymers and copolymers (depending on conditions) and hydrolyzes readily under mild acid or base conditions. This paper reports some of the synthesis, properties and applications performance of the homopolymers derivable from NVF and NVA.



Experimental

Solution Polymerization of NVF (NVA). One kg of vinylamide, 9 kg of H₂O and 11.5 g of AIBN (persulfate fails with both of these monomers) were adjusted to pH 8.5 with NH₄OH and polymerized under N₂ for 4 h at 60°C (pH readjusted to 8.5 as needed). Any acetaldehyde formed via hydrolysis of the monomer was removed before polymer hydrolysis by N₂ sparging. The resulting polymer showed $\bar{M}_n = 92,000$ and a polydispersity of 2.0 in 90% yield.

Inverse Emulsion Polymerization. Sorbitan monostearate (Span 60, 75 g) was dissolved in 2700 g of octane and N₂ sparged. NVF (450 g in 900 mL of H₂O, sparged with N₂) was added at 20 mL/min with vigorous agitation. The mixture was polymerized at 50°C with 1.5 g of Vazo 52 catalyst for 3 hr. The emulsion could be broken with acetone to give a polymer with $\bar{M}_w = 6.7 \times 10^6$ (via light scattering) and a Brookfield viscosity of 21,000 cps at a concentration of 5% in water. NVA was polymerized similarly using 15/45/90/4/0.08 NVA/water/xylene/Span 60/AIBN to give $\bar{M}_w = 1.5 \times 10^6$ by GPC.

Base Hydrolysis of PNVF. Aqueous PNVF was mixed with an equimolar amount of 50% aqueous NaOH and heated for 8 h at 60°C under N₂. The product was acidified and precipitated with concentrated HCl. Isolated and reprecipitated from water with MeOH. Alternatively, the free base may be precipitated from basic solution with acetone. PVAm-HCl, NMR (D₂O) δ 2.1 (br. s, 2), 3.7 ppm (br. s, 1); PVAm, NMR, δ 1.45 (br. s, 2), 3.05 ppm (br. s, 1).

Acid Hydrolysis of PNVA. Aqueous PNVA was mixed with two eq of conc HCl and heated at reflux for 27 h under N₂ (water added as needed). The polymer was precipitated with HCl and reprecipitated from water with MeOH.

Discussion

Monomer Properties. NVA is a white solid (mp = 50-55°C); NVF, on the other hand, is a distillable liquid (mp ~ -16 to -20°C, bp 84°C at 10 torr) with relatively low acute toxicity: LD₅₀(rat) = 1,444 mg/kg). NVF is quite stable for many months at room temperature when sufficiently pure. Less pure grades, however, are prone to degradation, usually via non-radical processes, and are best stored at lower temperatures.

Polymerization. Monomer conversion and polymer molecular weight are a strong function of monomer purity. Given good monomer quality, both NVA and NVF can be polymerized to high molecular weight. As with other monomers, chain transfer to solvent has a major impact on ultimate molecular weight. Isopropanol solution

polymerization can generate polyvinylamides with molecular weight below 10,000, while water solution polymerizations at high levels give polymers over one million molecular weight. S radical kinetics using inverse emulsion techniques give $\bar{M}_n \times 10^6$.

The best solvent for both PNVA and PNVF is water; solvents usually lead to a precipitation polymerization, part with NVF. Both NVF and NVA, however, are somewhat pro dependent hydrolysis in water, generating acetaldehyde, a chain transfer agent. Hydrolysis is adequately slow for NVF 6.5 and for NVA near pH 8 ($\pm 1-2$ pH units, depending on conditions).

Hydrolysis. PNVA can be hydrolyzed at reflux under acid. Strong base is also effective, but requires elevated temperatures in a pressure reactor. Homopolymer hydrolysis acid conditions slows dramatically at high conversions as charge repulsion becomes a major issue. Conditions to minimize this have been published [4].

A particular advantage of NVF is the ease of hydrolysis polymers. The homopolymer easily undergoes 60-80% hydrolysis under stoichiometric acid conditions and mildly elevated temperatures, but hydrolysis slows down due to charge repulsion when pushed to high conversion, except in the case of copolymer. Base hydrolysis suffers no such limitation and full hydrolysis obtained with near stoichiometric levels of hydroxide. Partial hydrolysis with water alone has also been observed at elevated temperatures under pressure.

Polymer Properties. Solution properties of unhydrolyzed or PNVA are much as would be expected by reference to polyacrylamide (PAM) of similar molecular weight (PNVF is an isomer of PAA). Hydrolyzed polymer is also initially unremarkable (Graph 1), but exhibits quite different properties as varied across a wider range (Graph 2, viscosity and protonation PVAm vs pH). PVAm shows very low viscosity at high pH - with largely unprotonated - but high viscosity in water at low pH. PVAm, as a result of significant charge repulsion in a polymer over 30% amine content, shows an extremely wide range of behavior as a function of extent of protonation. It thus functions as a buffer most of the pH range. In the critical pH 5-7 range, free base, cationic groups are roughly balanced: the polymer is both structurally cationic and has reactive primary amine functionality. Graph 2 reveals that the viscosity of PVAm is on the low side, but quite to other commercial water soluble polymers in 2% KCl at neutral pH.

Polymer Applications. Graph 3 shows the performance of PVAm in dewatering of a bentonite clay suspension. Although performance in flocculation is good, it is not clearly superior to polymers in this model system. The performance in dewatering, however, is very promising.

PVAm also shows excellent thermal and hydrolytic stability in water and high salt solutions. Potential applications for this polymer are shown below. In simulated oil well acidizing guar gum provides superior viscosity to PVAm in 10% HCl at 25°C. When the temperature is raised to 70°C, as in many deep wells, the guar undergoes rapid hydrolysis and fails. PVAm shows only a small temperature dependent drop in viscosity. In sea water, xanthan shows superior performance to PVAm and partially hydrolyzed, at 25°C, but both conventional polymers undergo rapid hydrolytic degradation at 90°C.

Oil Well Acidizing (0.5% polymer in 10% HCl)

	Visc (cps) @ 25°C	Visc (cps) @ 90°C
Guar Gum (Hitek C-15)	27	3
PVAm $\bar{M}_w = 7 \times 10^6$	22	15
*Fann 35, 300 rpm		

Low Shear Rheology* in Sea Water (3% NaCl, 0.3% CaCl₂, pH 11.5 (1500 ppm Polymer))

	Visc (cps) @ 25°C	Visc (cps) @ 90°C
Xanthan XC (Kelco)	49	3
PVAm $\bar{M}_w = 7 \times 10^6$	18	15
PAM $\bar{M}_n = 2 \times 10^6$ (Nalco, 30% Hydr.)	15	3
*Brookfield viscosity		

PVAm also shows excellent performance in the presence of divalent cations, which rapidly complex and precipitate partially

hydrolyzed anionic PAM. The table below shows good compatibility and viscosity in saturated monovalent and divalent salt solutions with PVAm, with viscosity improving, as expected, at higher molecular weight. This property is of importance in completion fluids for petroleum recovery.

Completion Fluids: Viscosity (cps) in Saturated Salt Solution (1g Polymer/100g Sol'n)		
	Sat'd NaCl	Sat'd CaCl ₂
PVAm $M_w = 7 \times 10^5$	11.5	300
PVAm $M_w = 6 \times 10^5$	3	100
Hydroxyethylcellulose-250 HHR (Hercules)	4	250

Another property which can be varied for PNVF or PNVA is extent of hydrolysis. As shown below, PVAm performs relatively poorly in minimizing fluid loss during oil well cementing. However, a partially hydrolyzed (about 20%), high molecular weight PNVF/PVAm is extremely close to the reference PEI polymer in this important parameter. (High formulation viscosity is, however, a potential problem.).

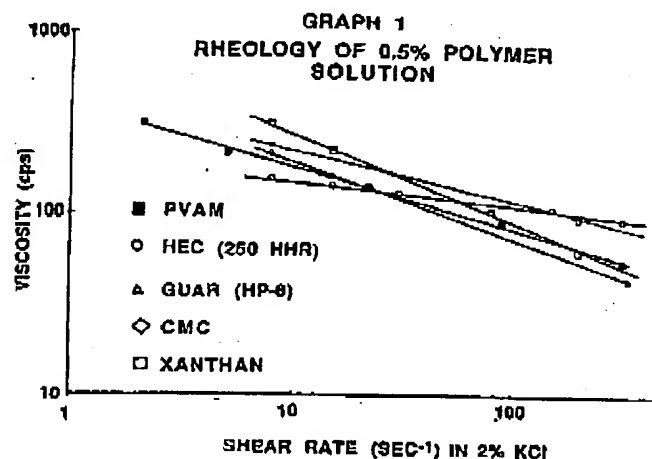
Fluid Loss Control, Type H Cement (860g+327g H ₂ O) (Polymer: 4.3g) Fluid Loss (mL @ 30 min) Visc (200rpm)		
PVAm $M_w = 6 \times 10^5$	45	300+
PVAm $M_w = 7 \times 10^5$	25	300+
PNVF/20%PVAm $M_w = 7 \times 10^5$	18	300+
Polyethyleneimine (Virginia Carcat P-800)	15	58

Polymer Reactivity. An additional advantage of polyvinylamines is that the amine groups are nicely reactive with a wide range of functionalities, as would be expected from monomeric analogs. PVAm in water can be crosslinked to a gel with aldehydes, epoxides, aminoplasts, many transition metals, polyvalent anions, Michael acceptors, and isocyanates at appropriate pH's.

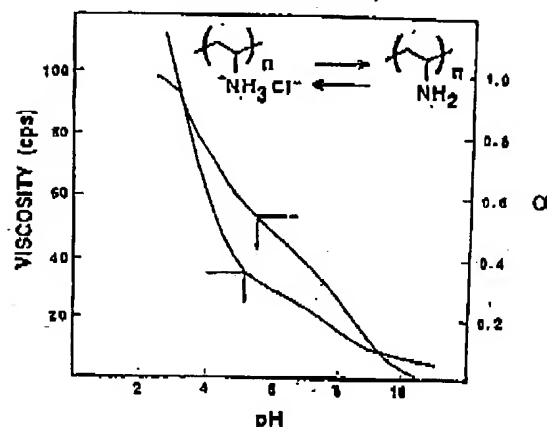
In conclusion, the two lowest members of the vinylamide series polymerize to high polymers and can be hydrolyzed, readily in the case of NVF, to polymer containing up to 32% NH₂ by weight. All of the forms are fully and readily water soluble. The hydrolyzed polymers show a wide range of basicities as a function of extent of protonation, due to charge repulsion effects, and have good stability in high salt, strong acid and elevated temperature environments. These properties suggest a wide variety of applications.

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- 4.



GRAPH 2
VISCOSITY AND % PROTONATION vs pH
(PVAm IN WATER)



GRAPH 3
DEWATERING OF BENTONITE CLAY

